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(19) (CA) **CANADIAN PATENT** (12)

(54) CARBOHYDRATE WASTES CONVERSION PROCESS AND APPARATUS  
THEREFOR

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ABSTRACT OF THE DISCLOSURE

There is described a process for pyrolytically converting carbohydrate-containing waste material such as straw, waste wood, garbage and manure into useful products such as gaseous and liquid hydrocarbons and alcohols. The process comprises:

- a) heating a mixture of calcium carbonate, and at least one alkali metal carbonate in a first reaction zone to a temperature in the range of 1200° - 1300°C. whereby the calcium carbonate is converted into CaO and CO<sub>2</sub>;
- b) introducing into a second reaction zone a feedstock comprising said carbohydrate-containing waste material in comminuted or pulverized form;
- c) simultaneously passing the reaction mixture resulting from said heating of CaCO<sub>3</sub> and alkali metal carbonate in said first reaction zone to said second reaction zone, said reaction mixture comprising a suspension of CaO and alkali metal carbonate; and intimately contacting said feedstock with said heated mixture therein; thereby effecting the decomposition of the feedstock into a mixture of carbon, hydrocarbons and gases including carbon monoxide and hydrogen; and at the same time during the course of the above reaction said CaO reacts with CO<sub>2</sub> therein to form CaCO<sub>3</sub>, said reactions in the second reaction zone occurring at super-atmospheric pressure;
- d) separating said gases from the mixture of CaCO<sub>3</sub>, alkali metal carbonate and carbon so formed, and withdrawing said gases from the second reaction zone;
- e) passing the withdrawn gases to a catalytic reactor wherein are formed said useable products;
- f) recycling said suspension of CaCO<sub>3</sub>, alkali metal carbonate and carbon to said first reaction zone; and
- g) repeating steps (a) - (f) above.

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Also described is apparatus for carrying out the above process. The apparatus includes (1) rectifier means within which the  $\text{CaCO}_3$  and alkali metal carbonate are converted to  $\text{CaO}$  and  $\text{CO}_2$ ; (2) pyrolysis means operatively connected to the rectifier means; (3) means for introducing carbhydrate-containing waste material feedstock into the pyrolysis means or reactor; (4) means for continuously cycling a suspension of solid material (e.g.  $\text{CaO}$  and carbonaceous material) in a fluid medium throughout the reactor and rectifier system; (5) means for withdrawing separated gases from both the reactor and rectifier; and (6) means for converting the separated gases withdrawn from the reactor into useable products such as hydrocarbon fuel and/or alcohols.

Carbohydrate Wastes Conversion Process and Apparatus Therefor

This invention relates generally to the conversion of waste materials into more useful products. More particularly, this invention relates to a process for the production of gaseous and liquid hydrocarbon fuel and chemical products such as methanol and fertilizer from carbohydrate containing waste materials such as cereal crop straw, waste wood, garbage and animal manure.

Processes are known for the conversion of such waste materials into other materials. For instance, it is known to subject sewage, garbage and the like to a pyrolytic treatment to obtain gases some of which may be used as fuel gases. An example of a process of this type is described in Canadian Patent 768,558 of Georg Borggreen, issued Oct. 3, 1967. Proposals have also been made to produce liquid hydrocarbons from carbonaceous materials, and one such proposal is described in U.S. Patent 3,597,327 of A.M. Squires, issued August 3, 1971. In Squires' process raw material such as coal or residual oil is pyrolyzed in the lower zone of a fluidized bed at a temperature of 900°-1700°F. Gaseous fuel products and coke or liquid fuels are produced. Another such process is described by Waterman in Canadian Patent 309,073 dated March 3, 1931.

In the process described in this patent, carbonaceous materials such as coal, cellulose, wood and the like is heated under pressure with hydrogen or hydrogen-containing gases or with substances yielding hydrogen in the presence of a catalyst comprising a mixture of hydrated iron oxide and hydrated aluminum oxide. A mixture of liquid hydrocarbons (which appear to be coal tar products), together with some water, is produced.

U.S. Patents 3,436,312 and 3,436,314 of Leonor, dated April 1, 1969, describe a process and apparatus for carbonizing vegetable waste materials, such as corn stalks, bagasse and the like, to form charcoal. In Leonor's process, combustible gases

and condensible vapors from preheating and carbonization stages are separated into acids, tars and gases which are used as heating fuel to enable the process to be autothermic, i.e. without requiring any external supply of heating fuel.

It is also known to convert lignocellulosic material into various chemical products by a pyrolytic process; one such process is described by Esterer in U.S. Patent 3,298,928, issued January 17, 1967, wherein sawdust or wood chips are pyrolytically converted into levoglucosan and carbohydrate-derived acids by  
10 heating in a gaseous medium at a temperature of from 600°-1500°F for a reaction period of not more than 30 seconds.

Zelnik et al in U.S. Patent 3,660,245, issued May 2, 1972, describe the continuous production of furfural and acetic acid from lignocellulosic material such as sawdust, and particularly apparatus for carrying out this process. The lignocellulose residue is burned to provide heat to carry out the reaction.

Albertson et al, in Canadian Patent 801,438, issued December 17, 1968 describe a method of disposing of wet organic waste material in which the waste matter is fed continuously  
20 into a combustion chamber, in the lower portion of which is a bed of substantial depth of inert granular material (e.g. sand) having heat-storing and heat-radiating capability, the material being maintained at a temperature between 1200° and 1800°F. A continuous upward stream of air is supplied into the bed through a constriction plate to keep the inert material in a fluidized state. It is to be noted that Albertson's method and apparatus are particularly devised so as to ensure that the waste material is completely combusted; there is no attempt made to recover  
30 products such as gases or fuels from the waste material.

Canadian Patent 809,948 of Mitsuru Tada, issued April 8, 1969 describes a method for continuously burning waste material containing both combustible and non-combustible material.

The waste material is charged into a furnace having a bed of a fluidized medium, in which combustion occurs of the combustible portion of the waste material; the fluidized medium and the non-combustible portion of the waste are removed from the combustion zone; separation of the non-combustible portion of the waste material from the fluidized medium is then effected; the fluidized medium is recycled to the combustion zone; and the non-combustible material is discharged. Again, there is no teaching or suggestion of converting the waste material into hydrocarbon fuel products.

10           In U.S. Patent 3,304,894 of Cox and McMullen, issued Feb. 21, 1967, there is described a method for converting refuse and trash into a fuel, in which the waste material is first reduced to a small particle size, after which it is dried, and then burned to produce a combustible fuel gas.

          The prior art processes mentioned above suffer from various disadvantages. For instance many known processes are inefficient, give low yields of desired products, and/or are inapplicable to treatment of all carbohydrate-containing waste materials, or are unsuitable for producing useful liquid products  
20   such as methanol or liquid hydrocarbons.

          The conversion of carbohydrate-containing waste materials to volatile gases or liquids by partial combustion, using a limited amount of air or by pyrolysis, involves severe heat transfer problems and results in a large amount of carbon dioxide in the product gas.

          It is an objective of this invention to provide an improved process for converting waste carbohydrate-containing material into useful products such as liquid hydrocarbons suitable for use as fuels, and alcohols.

30           A further, more specific objective of the present invention is a process for the pyrolytic conversion of such materials as straw, manure, waste vegetation, wood waste and

garbage into liquid hydrocarbon fuels and/or methanol.

Another objective of the present invention is the provision of a process for converting waste carbohydrate-containing material as aforesaid, in which all the products obtained from the process are useful; for example, a process in which, in addition to the recovery of liquid hydrocarbon fuels and/or alcohols, as products there are recovered the solid residues of the process for use either as fuel for process heat or for use as fertilizer.

10 Still another objective of this invention is the provision of apparatus, preferably apparatus which is mobile or portable, for carrying out the above process.

We have found that calcium carbonate together with some alkali metal carbonate such as  $K_2CO_3$  and  $Na_2CO_3$  can be heated in a suitable reactor to a temperature sufficient to convert the calcium carbonate to calcium oxide and further heated to the desired temperature for use in the conversion process.

20 At the required temperature it is injected and intimately mixed with the finely ground carbohydrate-containing feed stock in a reaction chamber. Since the resulting reaction is highly endothermic, the temperature of the media drop rapidly, causing the carbon dioxide to be absorbed by the  $CaO$ , leaving the carbon monoxide and hydrogen and some combined heavier hydrocarbon compounds which can be converted by catalytic action to useful liquid products and then separated by fractional distillation.

The present invention, in one broad embodiment, resides in a process for the pyrolytic conversion of carbohydrate-containing waste material to useable products including gaseous and liquid hydrocarbons and alcohols, which comprises the following steps:

- 30 a) heating a mixture of calcium carbonate and at least one alkali metal carbonate in a first reaction zone to a temperature in the range of  $1200^{\circ}$ - $1300^{\circ}$  whereby

calcium carbonate is converted into CaO and CO<sub>2</sub>;

- b) introducing into a second reaction zone a feedstock comprising said carbohydrate-containing waste material in comminuted or pulverized form;
- c) simultaneously passing the reaction mixture resulting from said heating of CaCO<sub>3</sub> and alkali metal carbonate in said first reaction zone to said second reaction zone, said reaction mixture comprising a suspension of CaO and alkali metal carbonate; and intimately contacting said feedstock with said heated mixture therein; thereby effecting the decomposition of the feedstock into a mixture of carbon, hydrocarbons and gases including carbon monoxide and hydrogen; and at the same time during the course of the above reaction said CaO reacts with CO<sub>2</sub> therein to form CaCO<sub>3</sub>; said reactions in the second reaction zone occurring at super-atmospheric pressure;
- d) separating said gases from the mixture of CaCO<sub>3</sub>, alkali metal carbonate and carbon so formed, and withdrawing said gases from the second reaction zone;
- e) passing the withdrawn gases to a catalytic reactor wherein are formed said useable products;
- f) recycling said suspension of CaCO<sub>3</sub>, alkali metal carbonate and carbon to said first reaction zone; and
- g) repeating steps (a) - (f) above.

According to another preferred embodiment of the invention, a process as described above is carried out, in which the relative proportions, by weight, of alkali metal carbonate to CaO are in the range of about 10:1 to about 48:1, there being



sufficient alkali metal carbonate to provide a liquid matrix for the CaO, and other solid materials, formed in the reaction occurring in said second reaction zone, the slurry so formed being maintained at a temperature of at least 900°C.

This invention, in another aspect, resides in a process as described hereinabove, wherein the reaction mixture comprising the CaO-containing suspension is in the form of a fluidized bed in each of said first and second reaction zones, the mixture being circulated by a flow of gas from the first reaction zone to the second reaction zone and vice versa.

In still another aspect, this invention resides in an apparatus for pyrolytically converting carbohydrate-containing waste material into useable products, which apparatus comprises:

- a) rectifier means containing a mixture of calcium carbonate and at least one alkali metal carbonate, said mixture having been heated to a temperature in the range of 1200°-1300°C. whereby it is converted to a suspension of solid material including CaO in a heat transferring fluid medium, said suspension being maintained in said rectifier means at said temperature, said rectifier means including means for heating the aforesaid mixture to said temperature of 1200°-1300°C, and maintaining said suspension at said temperature, and means for separating gases, including CO<sub>2</sub> from said suspension;
- b) means operatively connected to said rectifier means for the pyrolysis of carbohydrate-containing waste material in intimate contact with said suspension of CaO in a fluid medium, and for separation of gases produced by said pyrolysis from said suspension; said rectifier means (a) and said pyrolysis means (b) being maintained at superatmospheric pressure;

- c) means for introducing said carbohydrate-containing waste material feedstock in comminuted or pulverized form into said pyrolysis means;
- d) means associated with said rectifier means and said pyrolysis means for effecting continuous cycling of said suspension of solid material in a fluid medium to and from said rectifier means and said pyrolysis means;
- e) means for withdrawing the separated gases from said rectifier means;

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- f) means for withdrawing the separated gases from said pyrolysis means; and
- g) means for converting the separated gases thus withdrawn from the pyrolysis means into useable products.

In a further aspect, this invention resides in an apparatus as described above, in which:

the rectifier means and said pyrolysis means comprise two substantially vertically disposed tubular reactors in a parallel, spaced apart relationship, said reactors being  
10 lined with refractory material, each said reactor assuming the form of an inverted U, and each of said tubular reactors being filled to a predetermined level with a suspension of CaO and other solid materials in a fluid alkali metal carbonate matrix, said suspension being maintained at a temperature of at least 900°C; the relative proportions, by weight, of alkali metal carbonate to CaO being in the range of about 10:1 to about 48:1.

According to a further preferred aspect, the invention resides in an apparatus as described above, in which:

said rectifier means and said pyrolysis means comprise  
20 two substantially vertically disposed tubular reactors, each said reactor having: (a) a first substantially straight portion extending substantially vertically at least one-half the vertical height of said reactor; (b) a substantially vertically extending second straight portion substantially parallel to the counterpart portion of the other reactor, said second straight portion extending nearly the full vertical height of the reactor; said second straight portion being disposed outwardly of and substantially parallel to, said first straight portion and said second straight portions being also substantially parallel to each other;  
30 and (c) a third substantially straight portion integrally joined to said first straight portion at an obtuse angle, said third straight portion and said second straight portion integrally

merging with a curved portion at the top of the reactor, said third straight portion being inclined relative to said second straight portion at an acute angle;

said third straight portions of the rectifier reactor and the pyrolytic reactor having a spaced-apart, criss-crossing relationship to each other;

said first mentioned substantially vertically extending straight portion of each reactor constituting the main reaction zone thereof;

10 the lower end of said second straight portion of each reactor integrally merging with a short inwardly extending portion substantially perpendicular thereto, said inwardly extending portion connecting with the main reaction zone of the opposite reactor near the lower end thereof;

20 each of said reactors being filled to a predetermined level with a suspension of CaO and other solid materials in a fluid alkali metal carbonate medium, said medium being maintained at a temperature of at least 900°C.; the relative proportions, by weight, of alkali metal carbonate to CaO being in the range of about 10:1 to about 48:1.

In this specification the term "rectify" is used to refer to the purging of CO<sub>2</sub> (and any other wastes that may be removed) and the consequent conversion by heating of CaCO<sub>3</sub> to CaO; and the term "rectifier" is used to refer to the reactor in which this process takes place.

The terms "media" and "medium" ("media" being of course plural for "medium") are used in the same context and refer to the alkali metal carbonate - CaO mixture together with the solid products of the second reaction zone.

30 In the drawings which are attached to and form a part of this specification:

Fig. 1 is a graph illustrating the decomposition of calcium carbonate into CaO and CO<sub>2</sub> at temperatures in the range of 600°-900°C.;

Fig. 2 is a flowsheet illustrating the process according to one embodiment of the invention;

Fig. 3 is a flowsheet illustrating the process according to a second and preferred embodiment of this invention; and

Fig. 4 shows an alternative configuration for the reactor-rectifier used in carrying out the process illustrated by Fig. 3.

10 In the process according to the first-mentioned embodiment of the invention, as illustrated by Fig. 2, a dry granular medium is used, with a preponderance of  $\text{CaO}$ , with small amounts of alkali metal carbonate e.g.  $\text{Na}_2\text{CO}_3$  and/or  $\text{K}_2\text{CO}_3$ , mixed with it. The mixture is circulated by a flow of gas from the first to the second reaction zones and vice versa. In both reaction zones the reaction mixtures are in the form of fluidized beds.

20 By the "first reaction zone" we mean the reactor in which the calcium carbonate is heated to a temperature sufficiently high ( $1200^\circ\text{--}1300^\circ\text{C.}$ ) to decompose it into  $\text{CaO}$  and  $\text{CO}_2$  and wherein the  $\text{CO}_2$  is removed from the system, ie. the "rectifying" reactor or furnace. By the "second reaction zone" we mean the reactor in which the carbohydrate-containing wastes feedstock is admixed and reacted with the hot  $\text{CaO}$ -containing medium supplied from the rectifying reactor (or "first reaction zone") and wherein the feedstock is decomposed to yield gases comprising hydrogen and carbon monoxide.

30 Some of the carbon residue from the decomposition of the carbohydrate-containing wastes feedstock remains in the granular media and is returned with it to the rectifying furnace where its combustion provides a portion of the heat required for the expulsion of the carbon dioxide as well as conditioning for the return of the media to the reaction

chamber. The remainder of the heat required is provided by burning a portion of the product gas which also assists in fluidizing the media.

At temperatures above 1000°C, the yield is predominantly hydrogen and carbon monoxide, which can be synthesized to straight-chain saturated hydrocarbons or methyl and ethyl alcohol. At lower temperatures the yield consists of a mixture of heavy hydrocarbon compounds and water which can be separated by fractional distillation.

10 This embodiment of the invention will now be described in more detail with reference to Fig. 2.

Referring to Figure 2, the partially dried raw material is fed to a pulverizer mill 1 which pulverizes the feed stock to a fine granular material. It is then fed to a flash drier 2 which dries it to a controlled moisture content (eg. 26%-27% moisture by weight of the feedstock), and heats the material to a conditioning temperature before it enters the reactor. The material is then continuously fed to the fluid-bed pyrolyzer 3. Simultaneously, the rectified hot lime media and catalyst is fed from the rectifier furnace 4 at a controlled rate and temperature and is intimately flash mixed in the base of the fluid-bed pyrolyzer 3. Means (eg. tubes within which are enclosed oscillating screw feeders) are provided in both the feed channels to keep the media and the feed stock materials closely packed to prevent back flow of the generated gases from the pyrolyzer. As the mixture rises in the pyrolyzer the bed is kept fluid by the circulation of a portion of the product gas by blower 5.

20  
30 The product synthesis gases and condensable hydrocarbons are taken off to the heat exchanger 6 and then routed to fractional distillation columns or catalytic synthesis columns depending on the end products desired.

Some of the product fuel is used to supply heat to the rectifier furnace combustion chamber 7. Waste heat from both the heat exchanger 6 and the lime rectifier 4 is returned to the flash drier 2 where it is used for removal of excess moisture and for temperature-conditioning of the feedstock material.

In a second and preferred embodiment of the invention, the fluid-bed pyrolyzer and rectifier disclosed above is replaced by a special-purpose reactor operating at a higher pressure. This reactor is designed to yield products which can be processed to crude or semi-refined methanol, with by-products of medium oil and high phosphate fertilizer.

Before proceeding to a detailed description of this aspect of the invention with reference to Fig. 3, we shall outline the theory underlying the process, which is believed to provide a reasonably accurate picture of what occurs in said process. We wish to emphasize, however, that we do not wish to be bound by this theory.

The production of methanol from straw and carbohydrate-containing wastes is approximately described by the equation,



The weight relationship is:

$$90 \text{ lb.} + 342 \text{ lb.} \rightarrow 224 \text{ lb.} + 32 \text{ lb.} + 176 \text{ lb.}$$

Heat balance is:

$$0 + 2,222,000 \text{ btu.} - (890,000 + 1,967,000) + 0 = -635,000 \text{ btu.}$$

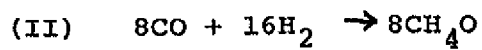
Sensible heat req'd, (as calculated on page 12, hereafter) is: 488,000 btu. Total heat req'd to satisfy equation (I) is:

$$635,000 \text{ btu.} + 488,000 \text{ btu.} = 1,123,000 \text{ btu.}$$

Temperature range is:

$$70^\circ\text{F to } 2,300^\circ\text{F or } 2230^\circ\text{F difference.}$$

The second stage conversion to methanol proceeds approximately in accordance with the equation:



Weight balance: 224 lb. + 32 lb.  $\rightarrow$  256 lb.

Heat balance:

$$\begin{aligned} 890,000 \text{ btu.} + 1,967,000 \text{ btu.} - 2,450,000 \text{ btu.} \\ = 407,000 \text{ btu.} \end{aligned}$$

Assuming that 60% of the sensible heat can be recovered for use in the first stage conversion, the net heat that would



have to be provided at the expense of the product would be:

$$1,123,000 - .6 \times (407,000 + 488,000) = 587,000 \text{ btu.}$$

per mole of straw. This represents a loss of 26.4 %.

The calculation of sensible heat for straw conversion now follows.

For  $\text{CO}_2$ ,  $C_p = 12 \text{ cal/g-mole } ^\circ\text{C} = 11.8 \text{ btu./lb-mole } ^\circ\text{F}$

For  $\text{H}_2$ ,  $C_p = 7.8 \text{ cal/g-mole } ^\circ\text{C} = 7.7 \text{ btu./lb-mole } ^\circ\text{F}$

For  $\text{CO}$ ,  $C_p = 22 \text{ cal/g-mole } ^\circ\text{C} = 6.05 \text{ btu./lb-mole } ^\circ\text{F}$

$$t_1 = 70^\circ\text{F}$$

$$t_2 = 2,300^\circ\text{F.}$$

$$t_2 - t_1 = 2230^\circ\text{F}$$

Sensible heat req'd per mole of straw is:

$$\text{CO} \quad 8 \times 6.05 \times 2230 = 108,000$$

$$\text{CO}_2 \quad 4 \times 11.8 \times 2230 = 105,000$$

$$\text{H}_2 \quad 16 \times 7.7 \times 2230 = 275,000$$

$$\underline{488,000 \text{ btu.}}$$

The volume of gas produced at 75 atmospheres and  $2300^\circ\text{F}$  per mole of straw is, to a good approximation for these conditions, 359 cu ft/lb-mole, so that for

$$\text{CO:} \quad 8 \times 359 \times \frac{2760}{530} \times \frac{1}{75} = 199 \text{ Cu ft.}$$

$$\text{CO}_2: \quad 4 \times 359 \times \frac{2760}{530} \times \frac{1}{35} = 100 \text{ Cu ft.}$$

$$\text{H}_2: \quad 16 \times 359 \times \frac{2760}{530} \times \frac{1}{75} = 399 \text{ Cu ft.}$$

$$\underline{698 \text{ Cu ft.}}$$

#### Heat transfer media calculations:

Considering the heat transfer media to have the specific heat of  $\text{Na}_2\text{CO}_3$

= .28 btu per lb. and it must transfer 1,022,000 btu, the ratio of the mass of media circulated per lb. of straw is

$$\frac{1,123,000}{.28 \times 342 \times 600} = 19.5 \text{ lb., where } \Delta T = 600^\circ\text{F}$$

is the overall temperature difference in the reactor column.

$\text{CaO}$  required per lb. of straw for reaction with  $\text{CO}_2$  is:

$$\frac{44}{56} \times \frac{176}{342} = .405 \text{ lb.: ratio of } \text{Na}_2\text{CO}_3:\text{CaO}$$

$$= \frac{19.5}{.405} = 48.2$$

Probable minerals trapped in the media per lb. of straw will be:

Sulphur	.007 to $K_2SO_4$	.039 lb.
Phosphorus	.025 to $NaPO_3$	.075 lb.
Sodium	.007	
Potassium	.005	
Calcium	.007	
Magnesium	.005	
Iron	.001	
TOTAL	.057 lb/lb	.114 lb.

$$P = 22\%$$

$$K = 4.38\%$$

It will be seen from Fig. 1 of the drawings that the dissociation pressure of  $CaCO_3$  decreases very rapidly as the temperature drops to  $900^\circ C$  or below. Therefore  $CaO$  present in the system will react with most of the  $CO_2$  present when the temperature drops to this value. At  $1200^\circ C$  calcium carbonate rapidly dissociates to  $CaO$  and  $CO_2$ . This is the reason why we employ granular  $CaO$  suspended in liquid alkali metal carbonate in our process.

The process according to this aspect of the invention features the use of molten alkali metal carbonate ( i.e.  $Na_2CO_3$  and  $K_2CO_3$  ) to form a liquid vehicle for a much smaller amount of  $CaO$  in granular form providing a  $CO_2$  absorbent. The relative proportions of  $Na_2CO_3$ ,  $K_2CO_3$  and  $CaO$  are not very critical. Sufficient  $Na_2CO_3$  and  $K_2CO_3$ , however, must be present to provide a liquid matrix for free circulation, and sufficient  $CaO$  must be present to absorb the excess  $CO_2$ . The proportion of alkali metal carbonate, expressed as  $Na_2CO_3$ , to  $CaO$  may range from about 10:1 to about 48:1.  $K_2CO_3$  can be substituted for  $Na_2CO_3$  in the same proportions, fluidity being the limiting factor of the lower range. The liquid alkali metal carbonate components also act as a heat

transfer medium.

Solids resulting from the pyrolysis of the feedstock i.e. char, are also suspended in the molten alkali metal carbonate medium and circulated in the slurry until completely reacted. Product ash also is suspended in the slurry.

Many other mineral compounds as mentioned previously herein for instance phosphates and sulphates, will accumulate in both types of media as end products of the feed stock. Because of this accumulation, some of the media must be continuously removed and replaced with new media. That is to say, dry granular media ( $\text{CaCO}_3$  and alkali metal carbonate) must be periodically fed into the pyrolysis reactor with the carbohydrate-containing wastes feedstock, and an equivalent amount of spent media drained off. The amount of carbonate added per lb. of feedstock will depend on the amount of fertilizer produced and on other factors such as viscosity and CaO loss to sulphates and other impurities. However, in general, fresh make-up carbonate is supplied to the pyrolysis reactor in an amount of from 1 to 2 percent by weight, based on the feedstock. The spent media can be reprocessed or used as fertilizer as is or in a refined form depending on market circumstances.

Since the methanol synthesis reaction in accordance with this process is best carried on at a pressure of 50 to 100 atm. and  $400^\circ\text{C}$ , considerable saving can be realized by carrying out the reaction wherein the carbohydrate-containing waste feedstock is decomposed at the same pressure. This involves compressing the straw feedstock into a solid tubular mass and extruding it into the reactor. In a particularly preferred aspect of the invention a combined liquid heat transfer and waste purging medium has been chosen initially to consist of approximately 48 lb. of  $\text{Na}_2\text{CO}_3$  to 1 lb.  $\text{CaO}$ .  $\text{K}_2\text{CO}_3$  and other products of the reaction occurring in the second reaction zone will rapidly mix with the original medium and fresh media will have to be intermittently exchanged. These waste media

is a natural fertilizer and should have market value. Since the melting point of this medium is  $870^{\circ}\text{C}$ , the minimum operating temperature will be  $900^{\circ}\text{C}$ .

These conditions can all be met in the reactor-rectifier herein described and the reaction in the pyrolysis reactor can be completely carried out at high pressure.

The invention will now be described in more detail, with reference to Fig. 3 of the drawings. Referring to Fig. 3, straw is chopped in chopper 10 to about 1 mm in length, with finer material intermixed, and is passed into the oscillating screw feeder 11 which presses it to a dense mass and extrudes the mass into zone A of the pyrolysis reactor 12.

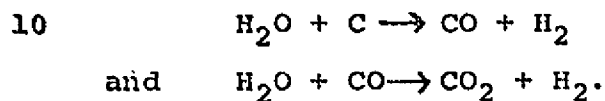
The reactor-rectifier consists of two inverted U-tubes; the left tube, 12, with zones A, C, D, and the right zone, 13, with zones B, F, E. When ready to operate, it is filled with liquid media at  $900^{\circ}\text{C}$  to the points marked (normal level). The tubes are lined with refractory material as shown by the dotted outline.

The two U-tubes, 12 and 13, are interconnected by cross tubes, 14 and 15. The pyrolysis reaction takes place in tube 12, and rectification takes place in tube 13.

The mixture of  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  (in the required proportions as previously indicated) present in tube 13 is heated to a temperature of  $1200^{\circ}\text{--}1300^{\circ}\text{C}$  ( $1250^{\circ} \pm 50^{\circ}\text{C}$ ). At this temperature the  $\text{CaCO}_3$  readily dissociates into  $\text{CaO}$  and  $\text{CO}_2$ . The  $\text{CaO}$  goes into suspension in molten alkali metal carbonate and this suspension is passed into the pyrolysis reactor 12.

Circulation of the media is up both tubes 12 and 13 and diagonally down the cross tubes 14 and 15. The circulation is driven by gases rising in both tubes 12 and 13 separating above zones C and F and the dense liquid flowing by gravity down the cross tubes. The media flowing up tubes 12 and 13 are gas-liquid

emulsions and the media flowing down cross-tubes 14 and 15 contain little or no free gas. The circulation of the media is aided by the difference in density between the gas-liquid emulsion and the dense liquid. The media therefore flows approximately in a figure 8. Gas in U-tube 12 is generated by the thermal breakdown of the extruded straw into synthesis gas and char. The char remains in suspension in the media and will react with the superheated steam the next time around in accordance with the water gas reaction;



It is believed that the alkali metal carbonates act as catalysts in this reaction.

Since the stage I reaction is highly endothermic, temperature of the media drops rapidly between zone A and zone C, and if properly regulated this drop will be approximately 300°C, bringing the media temperature to about 900°C. At this temperature the CaO suspended in the molten alkali metal carbonate will react with the CO<sub>2</sub> produced by pyrolysis of the carbohydrate-containing waste material feedstock to form CaCO<sub>3</sub>. The gas is  
 20 separated from the liquid media at zone C. The liquid flows down tube 14 and also can spill over port 16 and down tube 17. The synthesis gas then escapes up through zone D where any remaining media droplets are separated by the U-bend and baffle,  
 18.

Because of the endothermic reaction which occurs in reactor 12 it is necessary to supply heat to the system to maintain the temperature in both tubes 12 and 13 at the desired levels. The temperature is maintained by direct burning of a fuel-air mixture in zone B of U-tube 13 or by high frequency AC current  
 30 across the electrode pairs 24 in U-tube 13 and 25 in U-tube 12. Most of the heat must be supplied in U-tube 13, zone B, in order

to adequately purge the  $\text{CO}_2$ .

The synthesis gas then travels to heat exchanger 19, where the gas (comprising a mixture of  $\text{H}_2$  and  $\text{CO}$ ) is cooled to about  $400^\circ\text{C}$ ., and thence to condenser 20 and catalytic reactor 21 where it is formed into methanol, through control valve 22 and at atmospheric pressure through condenser 23.

Unreacted combustible gas is used to supply process heat and fuel for prime movers to drive compressors or electric generators connected with the system (not shown in the drawings).

The rectifier U-tube 13 is where the most of the heat is supplied in zones B and F, and if electrically heated, also across zone A in tube 12. The heat can be provided by a high frequency AC electric current across the water cooled electrode pairs 24 and 25, or it can be supplied by direct firing (injecting hot air and gas fuel at 26).

The hot gas rises with the media from zone B to zone F raising the media temperature to  $1300^\circ\text{C}$  and expelling the  $\text{CO}_2$ . The separation of the gas from the liquid phase is exactly similar to what was previously described for the reactor U-tube 12. The gas separation may be further encouraged by use of the apparatus illustrated in Fig. 4, as further described hereinafter.

Gas is expelled through zone E and around baffle 27 and passes into gas turbine 28. The turbine, 28, drives the turbocompressor, 29, which supplied high pressure air to the base of the rectifier, 13, into zone B. The exhaust gas can alternatively be passed through a heat exchanger and used to drive a steam turbine for the same purpose or an electric generator if electric heating is used.

Water is a necessary component of the reaction mixture in the pyrolytic reactor. normal moisture of the feedstock

Normal moisture of the feedstock may at most times be sufficient to supply the required water, but if not then extra water must be added either with the feed stock or as super-heated steam. The total water required is in a ratio of 90:342 or 26% by weight of the dry feed stock. Since 5 moles of water is needed for each mole of straw, much of the waste heat can be used to produce super-heated steam which is fed into the system at point 30 to partially char the straw and enter zone A for further reaction. As shown in Fig. 3, for this purpose steam at a temperature of 600°-800°C. and a pressure of 500-1000 psi. may suitably be used.

The reactor-rectifier is preferably operated at a pressure in the range of 50-100 atmospheres, and still more preferably, at a pressure of about 75 atmospheres. This is because the methanol catalytic reactor requires this pressure for good efficiency.

However, the reactor-rectifier will operate equally well at any pressure down to a few psi above atmospheric except that its size would have to be increased proportionally at lower pressures; and if used for methanol production the synthesis gas would have to be compressed to the required reacting pressure. This can be done by utilizing the sensible process heat for steam production and driving a steam turbo compressor to compress the synthesis gas.

A desirable feature of this invention is to produce mobile and portable processing apparatus to harvest the waste materials at their sites and so reduce transportation costs of raw materials. Since the use of low pressures would involve larger machinery size and greater weight, it is definitely preferred to use higher pressures of the order of 50-100 atmospheres, as aforesaid.

Discussion of Controls:

Operation of the Reactor-Rectifier depends on accurate, sensitive control.

The pressure in U-tube 13 must be held constant at say 75 atm. or 1125 psi  $\pm$  1 psi. Temperature in zones B and F must be held constant at 1250°C  $\pm$  50°C. Temperature sensing electrodes, 34 and 35 vary the gas-air mixture entering at 26 by the regulating valves, 36 and 37. Any change in position of these valves will cause a change in pressure in U-tube 13. If the pressure drops, it is sensed by electronic sensor 38 signaling fine-trimming control valve 31 to open wider thus increasing the pressure drop across gas turbine 28, increasing its speed and causing the turbo-compressor to increase its output thus restoring normal pressure. Excessive pressure will be corrected in exactly the reverse manner.

Pressure in U-tube 12 must be nearly equal to the pressure in U-tube 13; any difference is indicated by a difference in level of the fluid media and sensed by level sensors, 39 and 40. If the level is low, fine-trimming valve 33 is signalled to restrict gas flow, and if the level is high, valve 33 opens for less restriction. Valves 22 and 32 are for large adjustments beyond the range of the fine-trimming valves, 31 and 33. If the pressure balance becomes radically out of balance, say it is high in U-tube 12, the media level is forced down into zone A until the lower opening of tube 15 is exposed to the gas phase. At this point nearly all the liquid media will be in U-tube 13 and its upper surface will be at the high level mark in U-tube 13 sensed by the high level sensor, 40, and the low level sensor, 41. Synthesis gas can now escape up cross tube 15 to by pass tube 42 and exit at 27. Extreme low pressure in U-tube 12 will result in a similar procedure with waste gas travelling



up cross tube 14 and by-pass tube 17 exiting at 18. Equilibrium will be restored by correct response of control valves 32 and 22 and fine trimming valves 31 and 33.

Temperature control is accomplished as follows. The temperature of the liquid media leaving zone F should be  $1250^{\circ}\text{C} \pm 50^{\circ}\text{C}$ , and it should arrive at zone A at the same temperature or nearly so. If the proper ratio of media to straw feedstock (about 48:1 by weight) is maintained, the endothermic reaction in zone A will reduce the temperature in the rising column to  $900^{\circ}\text{C}$  in zone C. If the temperature difference is less than this, liquid flow is decreased by temperature sensors 43 and 44 signalling fine-trimming valve 33 to increase its restriction thus slightly increasing the pressure in U-tube 12 causing liquid level to drop slightly in zone C partly exposing the entrance of cross tube 14 and reducing the rate of liquid flow. This decreases the feed stock to liquid ratio, thus increasing the temperature difference between zone A and zone C. Too high a temperature difference will adjust valve 33 for less restriction causing the liquid level to rise in U-tube 12 to the point that more of the entrance opening at cross tube 14 is covered by fluid allowing an increase in fluid flow.

A suitable point for the removal of media is shown at 46 in cross tube 15, at which point there is placed a waste media port valve. Fluid removed here has travelled at least through one complete circulation cycle and while some unreacted carbonaceous product may be lost, it will be minimal.

Since there is considerable turbulence in the fluid media due to differential pressure fluctuations and the bubbling of gas rising through the fluid, the top surface boundaries will only be at the same level momentarily.

For instance, for normal level the fluid should simul-

taneously, at some instant, be in contact with level sensors 39 and 49; if not, the liquid volume is too low. Conversely, if at some instant the liquid is in simultaneous contact with, for example, level sensors 39 and 40, or 49 and 48, the liquid volume is too great and port valve 46 will automatically open and drain off sufficient liquid to restore the volume to the correct amount.

Monitoring of the level sensors by the use of an electronic logic device including the control of all regulating valves is imperative.

The choice of valves to be employed in the above-described system may be left to the discretion of the person skilled

in the art, wishing to practise this process and may be selected from among those well known types known in the art, and described for instance in the following references:

R.H. Perry and C.H. Chilton, Chemical Engineers' Handbook, 5th Edition (1973)

McGraw-Hill Book Co., Section 6, pp. 54-56 and Section 22, pp. 87-92;

Beard, "Final Control Elements" (1969) Chilton, Philadelphia Pa.;

Kallen, Handbook of Instrumentation and Controls (1961);

10 McGraw-Hill Book Co., Section 7, pp. 1-27 and 56-74; and

Crocker and King, Piping Handbook, 5th Edition, McGraw-Hill Book Co. (1967), Section 7, pp. 61-104.

Referring now to Fig. 4, of the drawings, there is shown a preferred configuration for the reactor-rectifier apparatus of the system illustrated in Fig. 3 and previously described.

All the functions in this alternative form of the Reactor-Rectifier are the same as tubes 12 and 13 shown in the flow sheet of Fig. 3 except that both the reactor tube 12 and the rectifier tube 13 have their upper portions zones C-D and F-E  
20 sloped at an angle. The angle can be 30° to 75° with 60° preferred. The reason for the sloping configuration is to facilitate more rapid gas separation from the liquid phase. As the gas liquid mixture rises in the sloping portion of the tubes, the gas tends to float to the upper sloped surface causing a difference in density between the upper and lower sides of the tubes. The dense fluid then flows downward to cross tubes 14 and 15 while the gas rises to zones E and D.

As will be seen from the foregoing description, for  
30 successful practice of the process of this invention several process parameters such as pressure, temperature and the amount of moisture supplied to the system with the feed must be scrupulously controlled. Adequate cooling of the exterior thereof must also

be provided. Generally, adequate refractory lining of the reactor-rectifier will ensure sufficient protection for the metal exterior, and cooling may be adequately provided by ambient air motion around the exterior surfaces. If desired, this air motion may be assisted by properly placed fans (not shown in the drawings). Cooling of the reactor-rectifier shell could also be effected by the passage of cooling liquid around its exterior by any suitable means (not shown in the drawings). The selection and disposition of circulating fans, or of suitable liquid cooling means about the reactor-rectifier, is well within the competence of those skilled in the art; and no further discussion of this is deemed necessary.

The body of the reactor-rectifier may be constructed of carbon steel or, if necessary or desired, of various alloy steels. The interior lining may be of magnesite or quartz. Other materials of construction for the reactor rectifier shell and/or for the refractory lining could also be used, provided the materials chosen have the necessary resistance to the temperatures encountered in the system, and the necessary chemical and corrosion resistance; generally speaking the selection of appropriate materials for these purposes can be made by the skilled artisan from among those known in the art and described, for instance, in Section 23 of Chemical Engineers' Handbook, 5th Edition (1973) McGraw-Hill Book Company.

As previously stated the carbohydrate-containing wastes feedstock is pulverized or comminuted before it is fed to the pyrolytic reactor. The degree to which the feedstock must be pulverized is variable to some extent depending on the nature of the material; but in general it must be pulverized to a degree of fineness that will compress to a sufficiently dense mass so that when extruded by the oscillating screw feeder, it will effectively prevent back flow of the gas in the reactor. For this purpose,

pulverization to an average particle size in the range of 0.1 to 0.5 mm. will in most cases be adequate.

While the present invention has been described herein in detail with reference to a preferred embodiment, it is to be understood that the invention is not to be limited thereto. For instance, the process is applicable to carbohydrate-containing waste materials other than straw, for example, garbage, animal manure, waste wood, paper, etc. As will be understood by those skilled in the art, process conditions may be varied to some extent, depending largely on the nature of the end products desired; and modifications may also be made in the apparatus used without departing from the aims and scope of the invention. It is desired, therefore, that this invention be limited only by the claims which follow.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the pyrolytic conversion of carbohydrate containing waste material to useable products including gaseous and liquid hydrocarbons and alcohols, which comprises:

a) heating a mixture of calcium carbonate, and at least one alkali metal carbonate in a first reaction zone to a temperature in the range of  $1200^{\circ}$  -  $1300^{\circ}\text{C}$ . whereby the calcium carbonate is converted into  $\text{CaO}$  and  $\text{CO}_2$ ;

b) introducing into a second reaction zone a feedstock comprising said carbohydrate-containing waste material in comminuted or pulverized form;

c) simultaneously passing the reaction mixture resulting from said heating of  $\text{CaCO}_3$  and alkali metal carbonate in said first reaction zone to said second reaction zone, said reaction mixture comprising a suspension of  $\text{CaO}$  and alkali metal carbonate; and intimately contacting said feedstock with said heated mixture therein; thereby effecting the decomposition of the feedstock into a mixture of carbon, hydrocarbons and gases including carbon monoxide and hydrogen; and at the same time during the course of the above reaction said  $\text{CaO}$  reacts with  $\text{CO}_2$  therein to form  $\text{CaCO}_3$ , said reactions in the second reaction zone occurring at super-atmospheric pressure;

d) separating said gases from the mixture of  $\text{CaCO}_3$ , alkali metal carbonate and carbon so formed, and withdrawing said gases from the second reaction zone;

e) passing the withdrawn gases to a catalytic reactor wherein are formed said useable products;

f) recycling said suspension of  $\text{CaCO}_3$ , alkali metal carbonate and carbon to said first reaction zone; and

g) repeating steps (a) - (f) above.

2. A process as set forth in Claim 1 wherein the

relative proportions by weight, of alkali metal carbonate to CaO are in the range of about 10:1 to about 48:1, there being sufficient alkali metal carbonate to provide a liquid matrix for the CaO and other solid materials, formed in the reaction occurring in said second reaction zone, the slurry so formed being maintained at a temperature of at least 900°C.

3. A process as defined in Claim 1 wherein the heating of material in said first reaction zone is effected by the combustion of an air-fuel gas mixture, said gas mixture being injected into said first reaction zone at its lower end.

4. A process as defined in Claim 2 wherein the heating of material in said first reaction zone is effected by the passage of a high frequency electric current across electrode pairs disposed at the lower end of said first reaction zone.

5. A process as in Claim 3 wherein gases are withdrawn from the upper end of said first reaction zone and a portion of said gases is mixed with air and recycled to provide the air-fuel gas mixture for heating said first reaction zone.

6. A process as in Claim 2 wherein the alkali metal carbonate is sodium carbonate, potassium carbonate or a mixture thereof.

7. A process as in Claim 2 wherein a portion of the suspension of solid material in the liquid alkali metal carbonate matrix is continuously removed and fresh make-up alkali metal carbonate and calcium carbonate is supplied to the second reaction zone.

8. The process of Claim 7 wherein said fresh make-up carbonates are supplied along with the carbohydrate-containing waste material feedstock.

9. A process as in Claim 1 wherein water is introduced into the second reaction zone.

10. The process of Claim 9 wherein the water is intro-

duced along with the carbohydrate-containing waste material feedstock.

11. The process of Claim 9 wherein the water is introduced into said second reaction zone in the form of superheated steam.

12. A process as set forth in Claim 2 wherein both of said reaction zones are maintained at a pressure in the range of 50 to 100 atmospheres.

13. A process as set forth in Claim 2 wherein the first and second reaction zones comprise parallel, vertically disposed, spaced apart, tubular reactors connected by two separate conduits extending diagonally of said reactors in a spaced apart, mutually intersecting relationship, and wherein the suspension of solid material in molten alkali metal carbonate matrix is continuously circulated from said first reaction zone to the second reaction zone and back to the first reaction zone via said diagonally extending conduits.

14. A process as in Claim 1 wherein the carbohydrate-containing waste feedstock is dried to a controlled moisture content of approximately 26% by weight of the material before introducing said feedstock into the second reaction zone.

15. A process as in Claim 2 wherein the gases withdrawn from the second reaction zone consist essentially of CO and H<sub>2</sub>, and said gases are cooled to about 400°C. and are then converted into methanol in a catalytic converter.

16. A process as in Claim 11 wherein the superheated steam is contacted with said carbohydrate-containing waste feedstock just before the latter is introduced into said second reaction zone.

17. A process as in Claim 1 wherein the carbohydrate-containing waste material serving as feedstock is comminuted or pulverized to a degree sufficient to allow compression to a dense



mass which effectively prevents back flow of gas from said reaction zone.

18. The process of Claim 17 wherein the carbohydrate-containing waste material is comminuted or pulverized to an average particle size of up to 1 mm.

19. A process as in Claim 17 wherein the comminuted or pulverized carbohydrate-containing waste material is compressed, by passage through an oscillating screw feeder, into a solid tubular mass which is extruded into said second reaction zone.

20. A process as set forth in claim 8 wherein fresh make-up alkali metal carbonate is supplied to the second reaction zone in an amount of approximately 1 to 2 percent by weight of the feedstock.

21. A process as set forth in Claim 1 wherein the carbohydrate-containing waste material is straw.

22. A process as set forth in claim 1 wherein the carbohydrate-containing waste material is waste wood.

23. A process as set forth in claim 1 wherein the carbohydrate-containing waste material is garbage.

24. A process as set forth in claim 1 wherein the carbohydrate-containing waste material is animal manure.

25. A process as defined in claim 1 wherein the reaction mixture comprising the CaO-containing suspension is in the form of a fluidized bed in each of said first and second reaction zones, the mixture being circulated by a flow of gas from the first reaction zone to the second reaction zone and vice versa.

26. A process according to claim 25 wherein the solid constituents of said suspension comprise a major proportion of CaO and a minor proportion of an alkali metal carbonate selected from the group consisting of  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and mixtures thereof.

27. A process as in claim 12 wherein the pressure in said first reaction zone is maintained at about 75 atmospheres.

28. A process as in claim 27 wherein the temperature in the first reaction zone is maintained substantially constant within the range of  $1250^{\circ}\text{C} \pm 50^{\circ}\text{C}.$ , and the pressure in the second reaction zone is maintained approximately equal to that in said first reaction zone.

29. A process as in claim 28 wherein variations in pressure in the first reaction zone and the second reaction zone from the desired values are compensated for by controlling the flow of gas to said first reaction zone and from said second reaction zone.

30. The process of claim 29 wherein variations in temperature in said first reaction zone from the desired value are compensated for by adjusting the liquid level of the heat transfer medium in said second reaction zone, thereby varying the ratio of heat-transfer medium to feedstock therein.

31. The process of claim 30 wherein when the liquid level rises above a predetermined value in said first and second reaction zones, a portion of the suspension of solid material in the liquid alkali metal carbonate matrix is withdrawn from the system until said liquid level is restored in said predetermined value.

32. Apparatus for pyrolytically converting carbohydrate-containing waste material to useable products, said apparatus comprising:

- a) rectifier means containing a mixture of calcium carbonate and at least one alkali metal carbonate, said mixture having been heated to a temperature in the range of  $1200^{\circ}\text{--}1300^{\circ}\text{C}.$ , whereby it is converted to a suspension of solid material including  $\text{CaO}$  in a

heat transferring fluid medium, said suspension being maintained in said rectifier means at said temperature, said rectifier means including means for heating the aforesaid mixture to said temperature of 1200°-1300°C., and maintaining said suspension at said temperature, and means for separating gases, including CO<sub>2</sub>, from said suspension;

- b) means operatively connected to said rectifier means for the pyrolysis of carbohydrate-containing waste material in intimate contact with said suspension of CaO in a fluid medium, and for separation of gases produced by said pyrolysis from said suspension; said rectifier means (a) and said pyrolysis means (b) being maintained at superatmospheric pressure;
- c) means for introducing said carbohydrate-containing waste material feedstock in comminuted or pulverized form into said pyrolysis means;
- d) means associated with said rectifier means and said pyrolysis means for effecting continuous cycling of said suspension of solid material in a fluid medium to and from said rectifier means and said pyrolysis means;
- e) means for withdrawing the separated gases from said rectifier means;
- f) means for withdrawing the separated gases from said pyrolysis means; and
- g) means for converting the separated gases thus withdrawn from the pyrolysis means into useable products.

33. Apparatus as defined in claim 32, wherein said rectifier means and said pyrolysis means comprise substantially vertically disposed chambers in a parallel, spaced apart relationship, said chambers being filled to a predetermined level in each chamber with said CaO-containing suspension of solid material in a fluid medium.

34. Apparatus as defined in claim 33 wherein the CaO-containing suspension of solid material in a fluid medium is in the form of a fluidized bed in each chamber.

35. Apparatus as defined in claim 34 wherein the solid constituents of said suspension comprise a major proportion of CaO and a minor proportion of an alkali metal carbonate selected from the group consisting of  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and mixtures thereof.

36. Apparatus as in claim 32 wherein said rectifier means and said pyrolysis means comprise two substantially, vertically disposed tubular reactors in a parallel, spaced apart relationship, said reactors being lined with refractory material, each said reactor assuming the form of an inverted U, and each of said tubular reactors being filled to a predetermined level with a suspension of CaO and other solid materials in a fluid alkali metal carbonate matrix, said suspension being maintained at a temperature of at least  $900^\circ\text{C}$ ; the relative proportions, by weight, of alkali metal carbonate to CaO being in the range of about 10:1 to about 48:1.

37. The apparatus of claim 34, wherein said means for effecting continuous cycling of said suspension of solid material in a fluid medium to and from said rectifier means and said pyrolysis means comprise two separate conduits extending diagonally of said reactors in a spaced apart, mutually intersecting relationship;

each of said conduits extending from one of said reactors at a point just below the predetermined level to which said reactor is filled with said suspension of solids in a fluid alkali metal carbonate medium, to the other reactor at a point adjacent the lower end thereof.

38. Apparatus as in claim 36 wherein the means for introducing carbohydrate-containing waste material into the pyrolytic reactor comprises an oscillating screw feeder which compresses said material into a solid mass and extrudes said mass into said reactor.

39. Apparatus as defined in claim 38 which includes also means connected to said oscillating screw 38 feeder for supplying water to said carbohydrate-containing waste material.

40. Apparatus as in claim 38 wherein the carbohydrate-containing waste material is straw, and there is included also means connected to said oscillating screw feeder for comminuting said straw to lengths of 1 mm. or less.

41. Apparatus as in claim 32 wherein said heating means comprises a chamber for combustion of a fuel gas-air mixture and means for injecting the hot gas mixture resulting from said combustion to the lower end of said rectifier reactor.

42. Apparatus as in claim 32 wherein said heating means comprise a pair of electrodes extending through opposite walls of said rectifier reactor, at the lower end of said reactor, said pyrolytic reactor also being provided at its lower end with a pair of electrodes similar to said first-mentioned electrode pair.

43. Apparatus as in claim 36 wherein said means for separation of gases produced by pyrolysis and element (f) comprise the inverted U-bend at the top of said pyrolytic reactor, a baffle mounted in said inverted U-bend of the reactor, and a gas withdrawal pipe connected to the top of said reactor.

44. Apparatus as in claim 36 wherein the gases withdrawn from the pyrolytic reactor consist essentially of CO and H<sub>2</sub>, and element (g) comprises, in sequence, a heat exchanger for cooling said CO and H<sub>2</sub> to a temperature of about 400°C., a condenser, and a catalytic reactor wherein said CO and H<sub>2</sub> are converted into methanol.

45. Apparatus as in claim 37 wherein the legs of each inverted U-tube are interconnected by a short duct at a point above said predetermined level to which the respective reactors are filled with the suspension of solids in the fluid alkali metal carbonate medium, and wherein the downcoming leg of each reactor tube is connected to a respective one of said diagonally extending conduits.

46. Apparatus as in claim 36 wherein said means for separating gases produced in said rectifier means and element (e) comprise the inverted U-bend at the top of said rectifier reactor, a baffle mounted in said inverted U-bend of said reactor, and a gas withdrawal pipe connected to the top of said reactor.

47. Apparatus as in claim 46 and having associated therewith a gas turbine into which the gas withdrawn from said reactor is passed.

48. Apparatus as in claim 36 and including means for maintaining the pressure in both of said reactors within the range of 50 to 100 atmospheres.

49. Apparatus as in claim 48 wherein said pressure-maintaining means comprise: means responsive to a change in pressure in said rectifier reactor and operative to increase the flow of gas to said reactor; and means responsive to a change in level of said suspension of solids in fluid alkali metal carbonate medium in the reactors, operative to control the flow of gas from said pyrolytic reactor.

50. Apparatus as in claim 48 wherein said temperature-maintaining means comprise: means responsive to a change in temperature in said rectifier reactor from the desired value and operative to control the fluid level of the heat-transfer medium in said pyrolytic reactor, and thereby control the ratio of heat-transfer medium to carbohydrate wastes feedstock therein.

51. Apparatus as in claim 36, and including means for continuously withdrawing a portion of the suspension of solid material in fluid alkali metal carbonate medium, and means for replenishing said alkali metal carbonate and calcium oxide in said suspension.

52. Apparatus as in claim 32, and including means for drying said waste carbohydrate-containing material feedstock to a controlled moisture content of approximately 26% by weight of the material.

53. Apparatus as in claim 32, and including means for pulverizing or comminuting the waste carbohydrate-containing material to a degree sufficient to permit compression of the feedstock to a dense mass.

54. Apparatus as in claim 53 wherein said pulverizing means is a hammer mill.

55. Apparatus as in claim 53 wherein said comminuting means is a chopper, said feedstock which is comminuted being straw.

56. Apparatus as in Claim 32, wherein said rectifier means and said pyrolysis means comprise two substantially vertically, disposed tubular reactors, each said reactor having:

- (a) a first substantially straight portion extending substantially vertically at least one-half the vertical height of said reactor;
- (b) a substantially vertically extending second straight portion substantially parallel to the counterpart portion of the other reactor, said second straight portion extending nearly the full vertical height of the reactor; said second straight portion being disposed outwardly of and substantially parallel to, said first straight portion, and said second straight portions being also substantially parallel to each other; and (c) a third substantially straight portion integrally joined to said first straight portion at an obtuse angle, said third straight portion and said second straight portion integrally merging with a curved portion at the top of the reactor, said third straight portion being inclined relative to said second straight portion at an acute angle;

said third straight portions of the rectifier reactor and the pyrolytic reactor having a spaced-apart, criss-crossing relationship to each other;

said first mentioned substantially vertically extending straight portion of each reactor constituting the main reaction zone thereof;

the lower end of said second straight portion of each reactor integrally merging with a short inwardly extending portion substantially perpendicular thereto, said inwardly extending portion connecting with the main reaction zone of the opposite reactor near the lower end thereof;



each of said reactors being filled to a predetermined level with a suspension of CaO and other solid materials in a fluid alkali metal carbonate medium, said medium being maintained at a temperature of at least 900°C; the relative proportions, by weight, of alkali metal carbonate to CaO being in the range of about 10:1 to about 48:1.

57. Apparatus as in claim 56, wherein, in each reactor, said third straight portion of said second straight portion are interconnected by two conduits, each conduit extending perpendicularly of said third straight portion and diagonally of said vertically extending straight portions.

58. Apparatus as in claim 56 wherein said third straight portion of each reactor is inclined relative to the second straight portion thereof, at an angle of 30° to 75°.

59. Apparatus as set forth in claim 58 wherein the angle of inclination is 60°.

60. Apparatus as in claim 37, wherein means are provided in one of said diagonally extending conduits interconnecting the tubular reactors, for continuously withdrawing a portion of the suspension of solid material in the fluid alkali metal carbonate medium.

61. Apparatus as in claim 50 and further comprising: means responsive to said fluid level controlling means and operative to permit withdrawal of a portion of the suspension of solid material in the fluid alkali metal carbonate medium until the fluid level of the heat-transfer medium is restored to said predetermined level in the reactor and rectifier.

62. A process according to claim 14 wherein said drying of the carbohydrate-containing waste feedstock to said controlled moisture content is effected in a flash drier, said

flash drier also being used to heat said carbohydrate-containing waste feedstock to a conditioning temperature prior to its introduction into said second reaction zone.

63. A process according to claim 62 wherein waste heat from the first and second reaction zones is supplied to said flash drier for removal of excess moisture from the feedstock and for temperature conditioning of said feedstock.



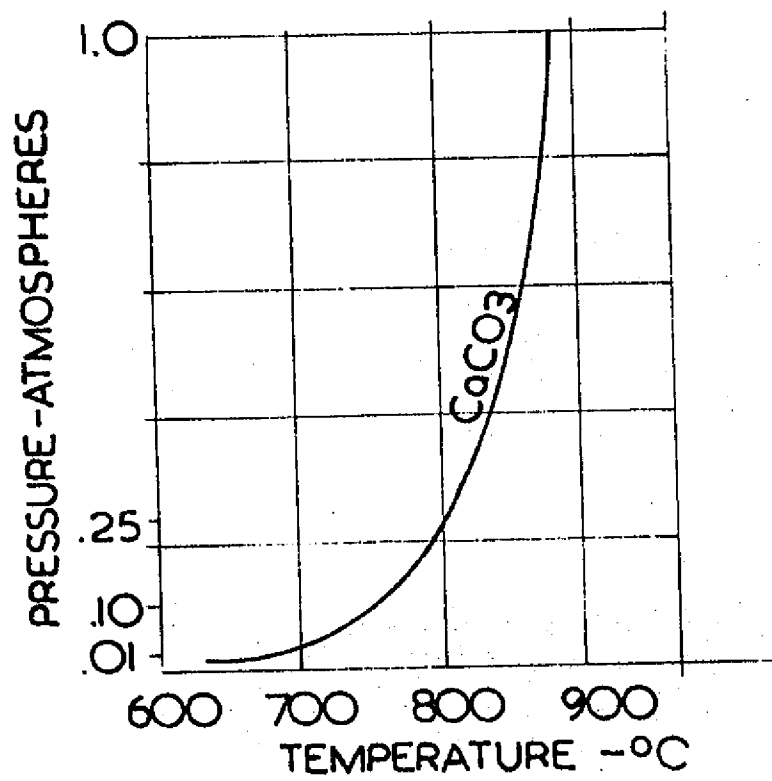
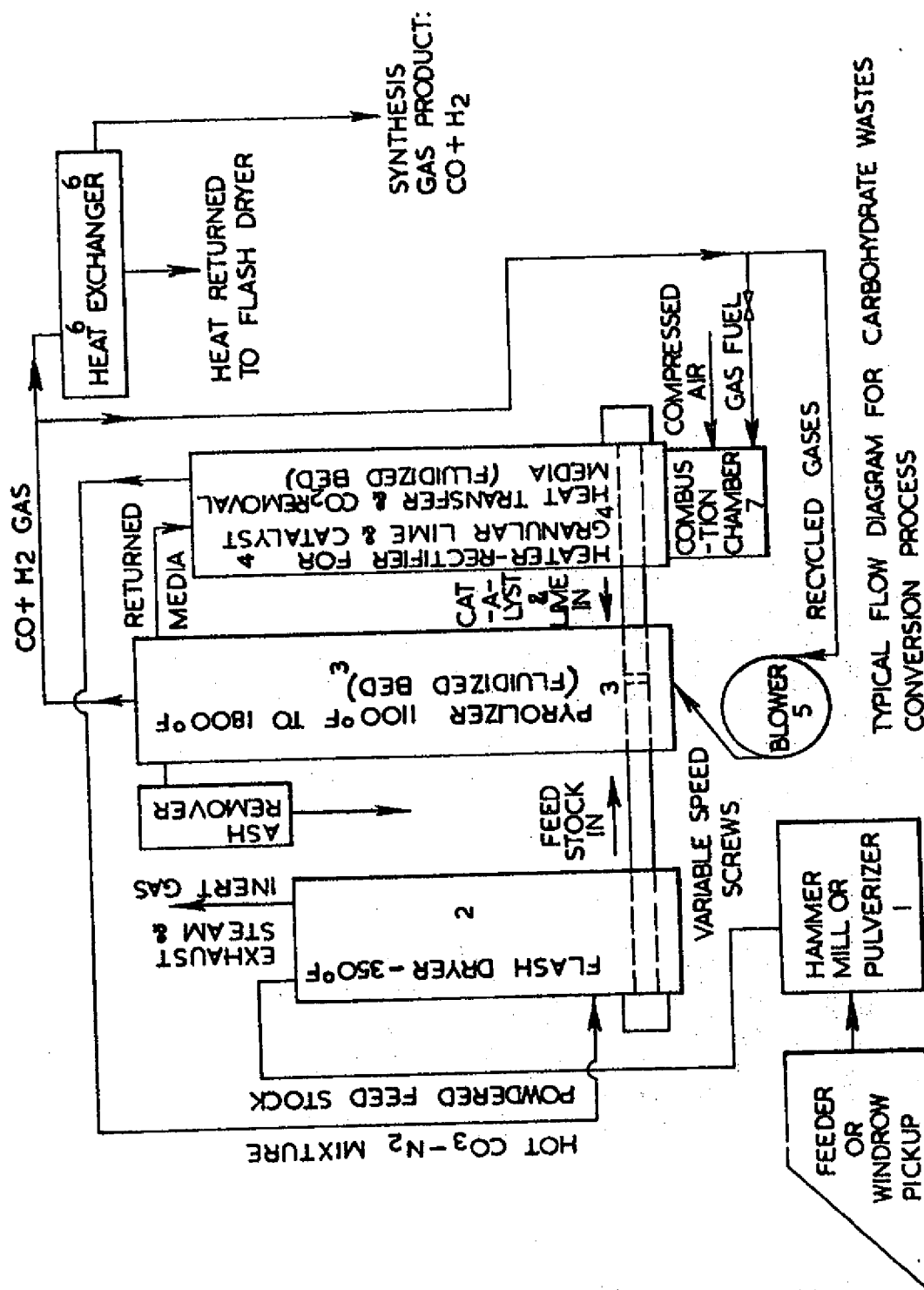


FIG. 1.



TYPICAL FLOW DIAGRAM FOR CARBOHYDRATE WASTES  
CONVERSION PROCESS

FIG. 2.

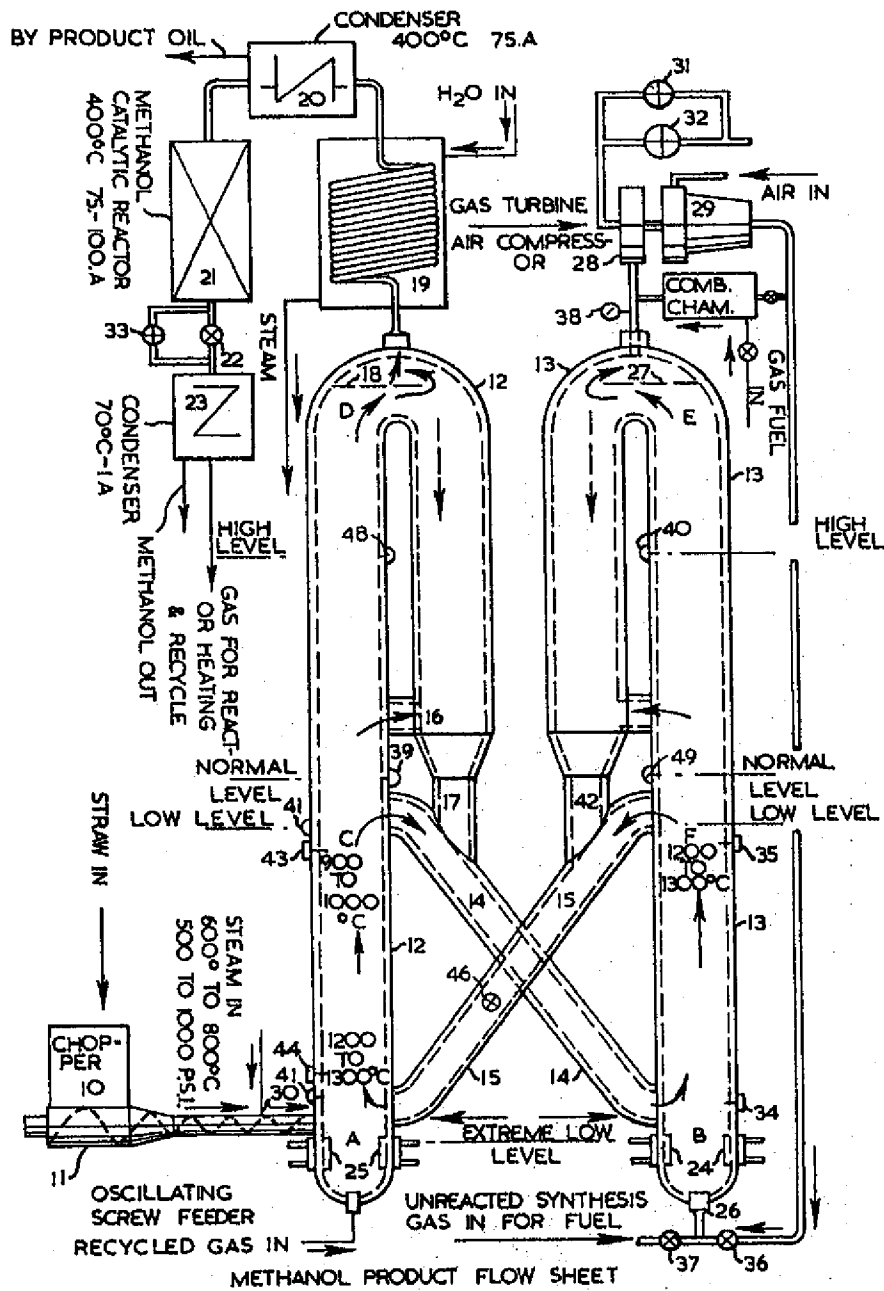


FIG. 3.

